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Application of FWAs for High Brightness, High Yield Pulps

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ABSTRACT

This paper examines the photostabilization effects of a diaminostilbene-based fluorescent whitening agent (FWA) for hardwood BCTMP. The use of a 0.1–0.5% charge of the FWA onto handsheets of BCTMP was shown to retard photoyellowing by 25%. The use of polyethyleneglycol was shown to improve the photostabilization effects of the FWA presumably by improving the surface coverage of the FWA onto the fiber. Brightness measurements excluding the fluorescent component of the FWA treated BCTMP handsheets suggest the fluorescent whitening agent is most effective in retarding the slow phase of brightness reversion. The use of an antioxidant in conjunction with a FWA was found to improve the overall photostability of BCTMP.

Application: The use of FWA with a BCTMP or BCTMP-kraft furnish is shown to reduce the photoyellowing properties of paper containing high yield pulp.

The manufacturing of mechanical pulp for papermaking is an attractive and efficient utilization of wood resources. With average pulp yields exceeding 85% and the ability to prepare pulps with +85 brightness, this fiber is a viable resource for many papermaking applications *(1)*. Unfortunately, the well-known tendency of mechanical pulps to undergo rapid photoyellowing has limited their applications *(2)*. Studies by Cockram suggest that if brightness losses of CTMP could be limited to less than 3% over 3–12 months, usage of this valuable furnish would increase

2 to 6 fold *(3).*

Early investigations by Leary *(4)* and others *(5,6)* clearly demonstrated that absorption of near UV light (λ= 300-400 nm) by the lignin component of mechanical pulp, in the presence of oxygen, leads to photoyellowing of mechanical pulp. A variety of other factors, such as pH *(7)*, metal salts *(8)*, bleaching *(9, 10, 11)*, moisture content *(7)*, and resin content *(12)*, have been examined to determine their role in the brightness reversion phenomenon. These investigations have not been successful in finding manufacturing conditions that significantly reduce the rate of photoyellowing for mechanical pulps.

To date, investigators have examined four technologies to retard or halt the overall rates of photoyellowing of mechanical pulps including: chemical modification of mechanical pulp, coating with inert additives, addition of UV absorbers, and addition of antioxidants *(13).* Chemical modification of mechanical pulps has provided some of the most effective methods of photostabilizing high yield pulps. Indeed, Magnus and Ragauskas demonstrated that acylation of aspen BCTMP yielded a sheet that could retain full brightness in excess of 400 hours of continuous irradiation *(14, 15)*. Unfortunately, the technology needed to apply this process for mill usage remains yet to be developed.

The application of photostabilization additives to mechanical pulp has developed rapidly over the past decade. Cole et al. *(16),* Janson and Forsskahl *(6)*, Maiocchi et al. *(17)* and Minemura and Umehara *(18)* have demonstrated the benefits of polyethylene glycol as a photostabilization agent for mechanical pulps. Hortling et al. *(19)* and Janson et al. *(20)* have demonstrated that polyvinylpyrrolidone and polytetrahydrofuran retard the photoyellowing rates of PGW and CTMP.

The use of radical scavenging agents and other antioxidants to retard the photoyellowing of high-yield pulps has seen increasing scientific investigation *(21, 22, 23)*. Perhaps the greatest difficulty posed by this approach has been the gradual loss of the additive to thermal autoxidation reactions.

One of the simplest and most effective means of photostabilizing mechanical pulps is by the addition of a UV absorber that prevents light in the 300-400 nm range from interacting with lignin. Studies by Nolan *(24)*, Kringstad *(25)*, and Fonier de Violet et al. *(26)* have demonstrated the effectiveness of several substituted 2-hydroxybenzophenone derivatives (see Fig. 1) at retarding brightness reversion. Davidson et al. have demonstrated that benzotriazole derivatives, another class of UV absorbers, are also effective in hindering photoyellowing *(27)*. To extend the observed photostabilization effects of UV absorbers, Pan et al. have examined the use of additive mixtures *(28)*. By employing mixtures of UV absorbers and radical scavengers, the overall rates of brightness reversion could be decreased by approximately 50% while reducing the charge of individual additives by a factor of two or greater. Despite these advances, the amounts of UV absorbers required to significantly retard the photoyellowing of mechanical pulp have hindered their commercial application.

Of the many chemical technologies that have been explored for mechanical pulps, one of the least studied is fluorescent whitening agents (FWA). The use of a FWA provides a two-fold benefit for mechanical pulps, as these additives will enhance the initial brightness of a treated sheet and act as a UV-screen. A recent study by Muller suggested economic benefits could be incurred if FWAs were employed with CTMP pulps to improve apparent brightness values *(29)*. Doshi has reported that FWAs will not brighten groundwood pulps as lignin can act as a quencher but suggested that this technology would be suited for CTMP and BCTMP grades of pulp to achieve higher brightness values *(30)*. Recently, Bourgoing and Robert presented results suggesting that FWAs could be used to retard the photoyellowing of TMP *(31)*. In this report we wish to describe our efforts at retarding the photoyellowing properties of high brightness BCTMP treated with a FWA and exposed to office lighting.

EXPERIMENTAL

Materials

All chemicals and reagents including the fluorescent whitening agent: 2,2-(1,2-ethenediylbis(3-sulfo-4,1-phenylene)imino(6-diethylamino)-1,3,5-triazine-1,2-diyl(imino))bis-1,4-benzene-disulfonic acid, hexasodium salt (FWA1, see **Fig. 1**), polyethylene glycol (MW:8,000) and polytetrahydrofuran (MW:250) were commercially purchased and used as received. Commercial hardwood BCTMP and fully bleached softwood kraft pulp were employed for all studies. The

BCTMP was prepared employing hydrogen peroxide for the chemical impregnation and bleaching stages.

Preparation of pulps and handsheets

Prior to usage of the BCTMP, the pulp was refluxed in distilled water for 20 min at 2% consistency. The pulp was then filtered and used to prepare handsheets (60 g/m^2) following TAPPI standard procedure T 205 om-88 employing either 100% BCTMP or 50% BCTMP, 50% kraft as a furnish.

Handsheets of BCTMP or 1:1 BCTMP-kraft were sprayed with a methanolic solution (10.0 mL) of the photostabilization additive. The handsheets were then allowed to air dry overnight in the absence of light.

Photoaging Studies

The treated and untreated handsheets were stored 2 m from a series of four fluorescent office lights. The handsheets were removed from the light source approximately every 3 days, and their optical properties were determined following standard TAPPI procedures. Reported brightness values represent the average of four separate measurements, typically these brightness varied less than 2%.

RESULTS AND DISCUSSION

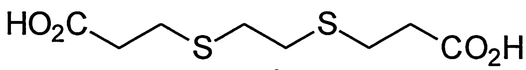
As a preliminary investigation, a commercially available FWA was applied onto handsheets of 100% hardwood BCTMP or a 1:1 mixture of hardwood BCTMP/bleached softwood kraft pulp. The treated and untreated handsheets were then simultaneously irradiated with office lights and TAPPI brightness measurements were taken periodically. The results of the photolysis experiments are summarized in **Figure 2**. The treated handsheets exhibited an initial brightness gain due to the FWA and, upon irradiation, the treated sheets continued to exhibit higher brightness values and a reduced rate of photoyellowing.

The photoaging dose response of FWA1 was explored with a series of BCTMP and BCTMP/kraft handsheets. **Figures 3–4** summarize the results of these studies. These results suggested that the optimal FWA1 charge for BCTMP handsheets was approximately 0.5%(w/w).

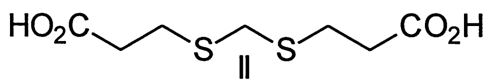
Indeed, the use of a 1.0% charge of FWA1 gave lower photostabilization effects than a 0.5% charge and this was attributed to the graying limit of the FWA. It is well known that when the surface fiber bonding properties for a fluorescent whitening agent are saturated the FWA will associate with itself. This effect prevents further "whitening" and a so-called graying limit is reached. Interestingly, handsheets prepared from 50% kraft and 50% BCTMP appeared not to suffer from the same graying limit (see **Fig. 4**). Presumably, insufficient FWA1 was added to the handsheet prepared from BCTMP/kraft to reach the graying limit. The nature of these differences between 100% BCTMP and mixtures of BCTMP/kraft handsheets remains to be established.

The use of a carrier molecule has been frequently reported to improve the optical properties of FWAs. It is hypothesized that molecules such as polyethylene glycol, polyvinyl alcohol, and carboxymethylcellulose can assist in distributing the FWA agent onto the surface of a fiber. To explore this issue, we impregnated a series of 1:1 BCTMP/kraft handsheets with FWA1 and PVA, carboxymethylcellulose, or polyethylene glycol. The most effective carrier molecule was determined to be polyethylene glycol (2%) which decreased the overall rate of reversion by 45% with respect to BCTMP handsheets treated solely with FWA1 as shown in **Figure 5**. Based upon our previous reversion studies on PEG, it is clear that the observed photostabilization effects must be due to an improved application of FWA1 on the surface of the pulp fiber, since the known photostabilization effects of PEG require much higher application levels.

Additional improvements in the photostabilization properties of FWA1 were observed when a second additive was applied to the sheet. Amongst the additives studied, we observed improved FWA1 photostabilization effects using 3-(2-(2-carboxyethythio)ethythio)propanoic acid (I), 3-(2-(2-carboxyethythio)methylthio)propanoic acid (II), 3-sulfanylpropanoic acid (III) or polytetrahydrofuran (IV) as a second photostabilization agent.



I



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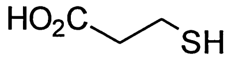

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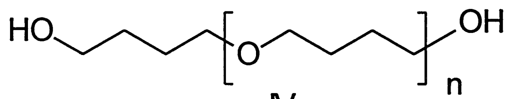

IV

Figure 6 summarizes the photostabilization effects observed when a combination of these additives were applied to a 25% BCTMP/75% kraft handsheet. Although the use of FWA1 and polytetrahydrofuran provided the best photostabilization effects, all the additives provided comparable improvements in retarding the overall rates of brightness reversion. An alternative means of measuring the effects of the FWA is to monitor TAPPI brightness excluding the fluorescent component of the fluorescent whitening agent. The results of these measurements for FWA1 and the co-additives are shown in **Figure 7**. These results clearly suggest that the FWA additive has a more pronounced effect on the slow phase of brightness reversion than the initial fast phase of photoyellowing.

In summary, the photostabilization benefits observed with FWA1 treated BCTMP handsheets are undoubtedly associated with its mechanism of brightening. It is well known that fluorescent whitening agents absorb light in the 340–380 nm spectral region and then emit blue light in the 425–450 nm region. In this process, FWAs absorb harmful near-UV light and remit light in the visible range giving the mechanical pulp the appearance of higher brightness. Furthermore, it is known that mechanical pulps undergo photobleaching upon exposure to 400–450 nm light and the addition of a FWA could potentially retard photoyellowing by contributing to this photobleaching effect. Further research is needed to determine if photobleaching is actually enhanced in the presence of a FWA.

CONCLUSION

The use of fluorescent whitening agents to hinder brightness reversion of mechanical pulps appears to be a promising technology for high yield pulps. We have demonstrated that the effects of FWA can be improved with the addition of a carrier molecule and with other photostabilization technologies. These results and a recent report by Bourgoing and Robert on the photo-stabilization of TMP pulps with FWA suggest that these additives may provide an effective technology for retarding the photoyellowing of mechanical pulp *(31)*. Clearly, additional studies are needed to identify alternative co-additives and other potential FWAs that will improve the overall photostabilization effects for high yield pulps. Studies directed at addressing these issues are ongoing.

ACKNOWLEDGMENTS

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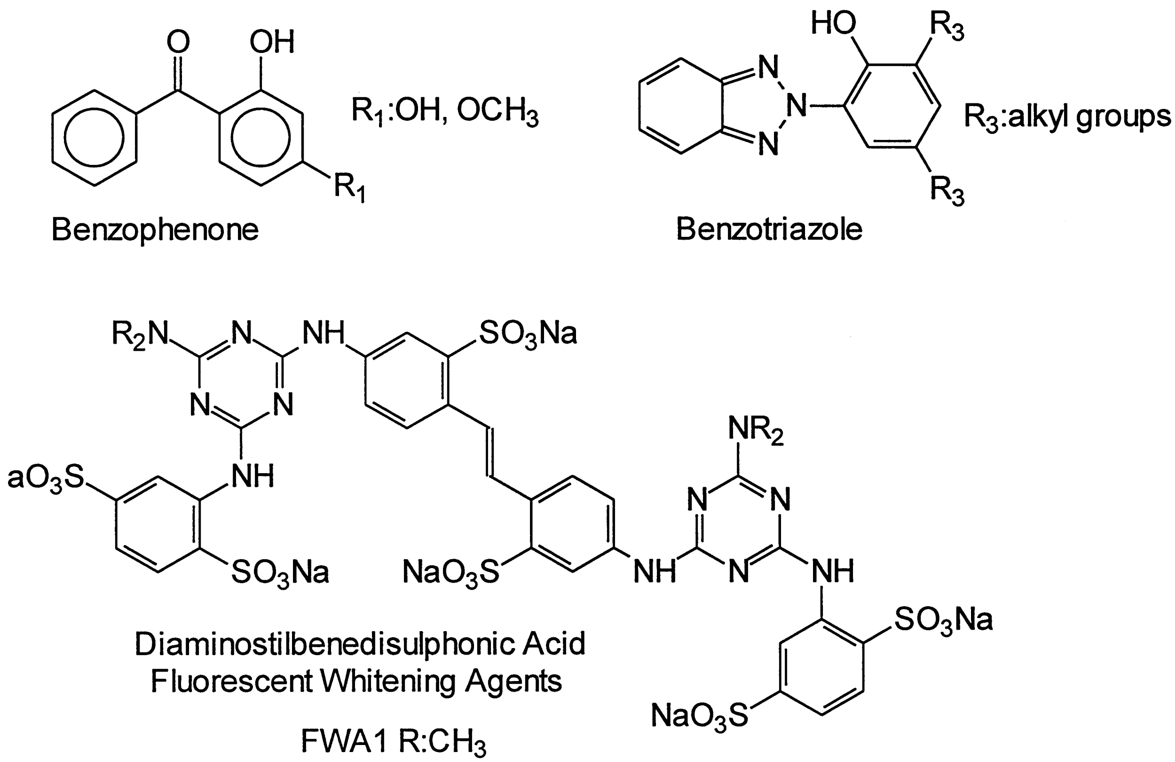
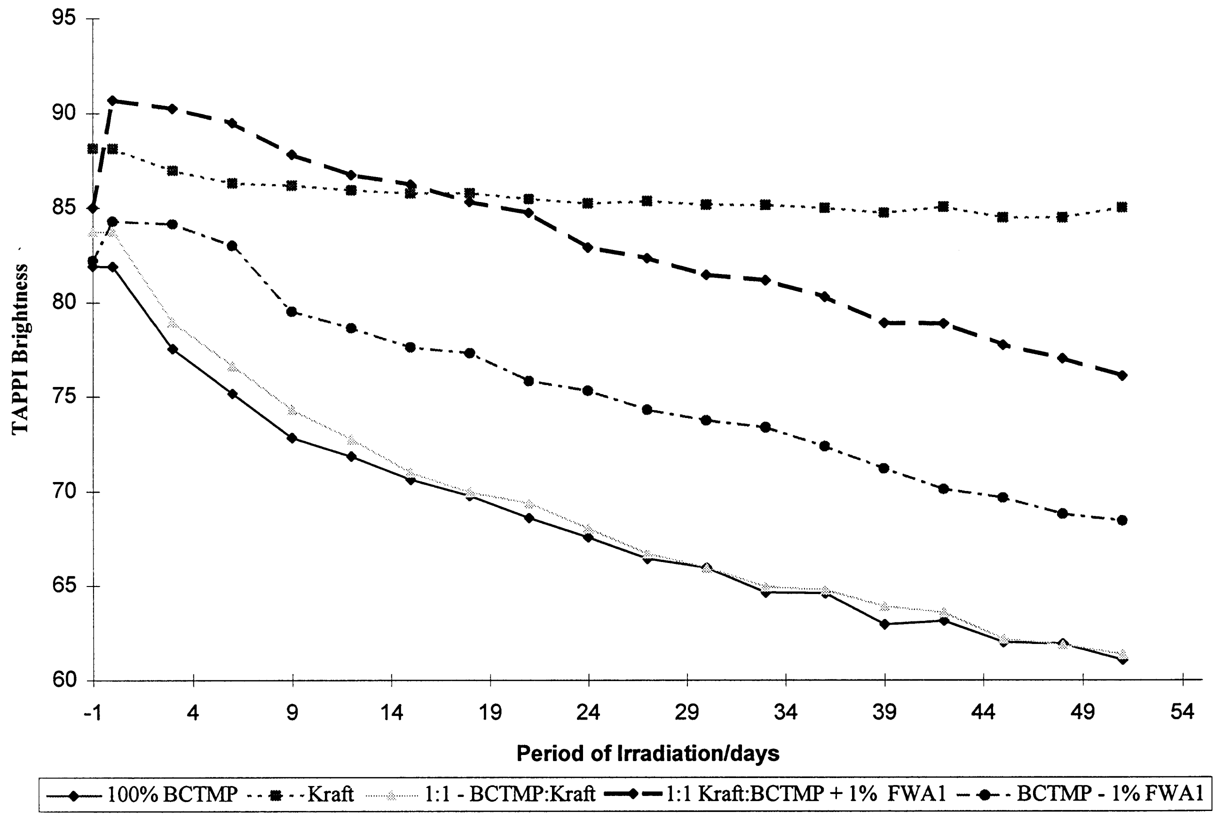


Figure 1. Typical additives for the absorption of 300–400 nm light.



Note: -1 Period of irradiation denotes brightness values prior to additive treatment.

Figure 2. Photoreversion of treated and untreated 100% HW BCTMP and 1:1 HW BCTMP/SW kraft handsheets.

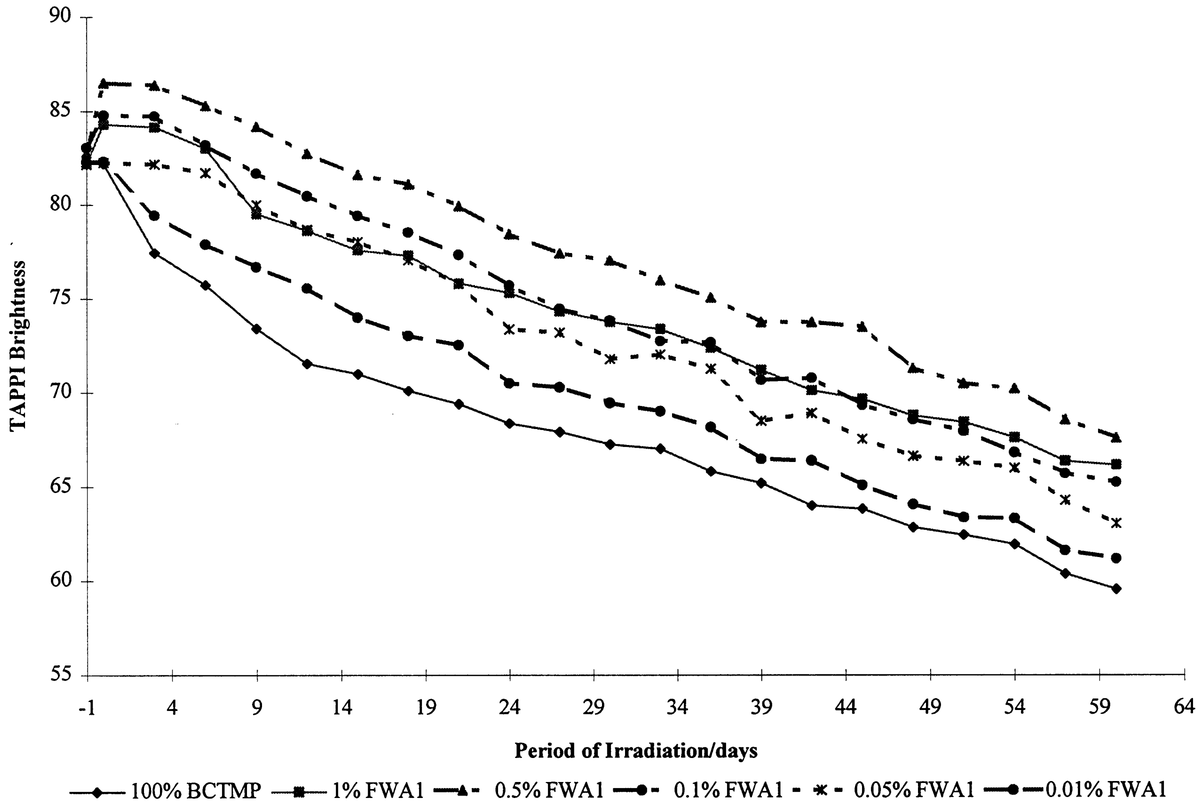


Figure 3. Photoreversion properties of HW BCTMP handsheets treated with FWA1.

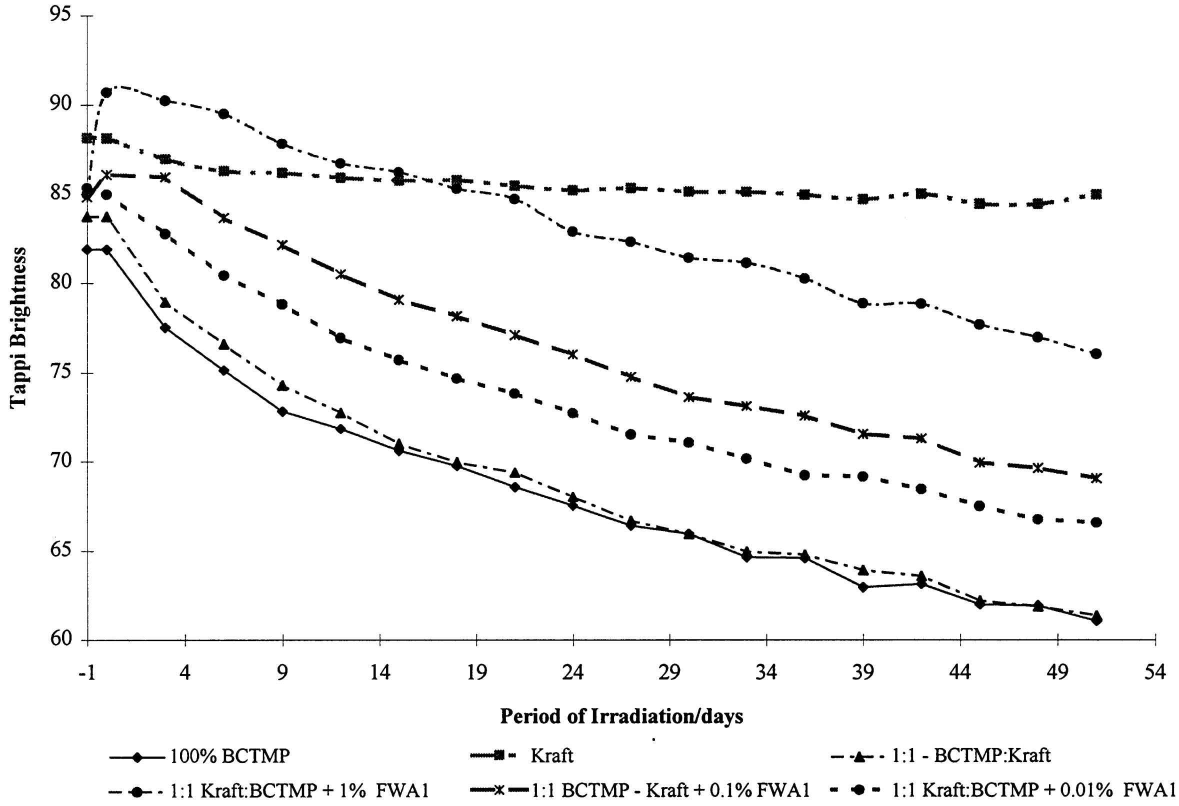


Figure 4. Photoreversion of 1:1 HW BCTMP/SW kraft handsheets treated with FWA1.

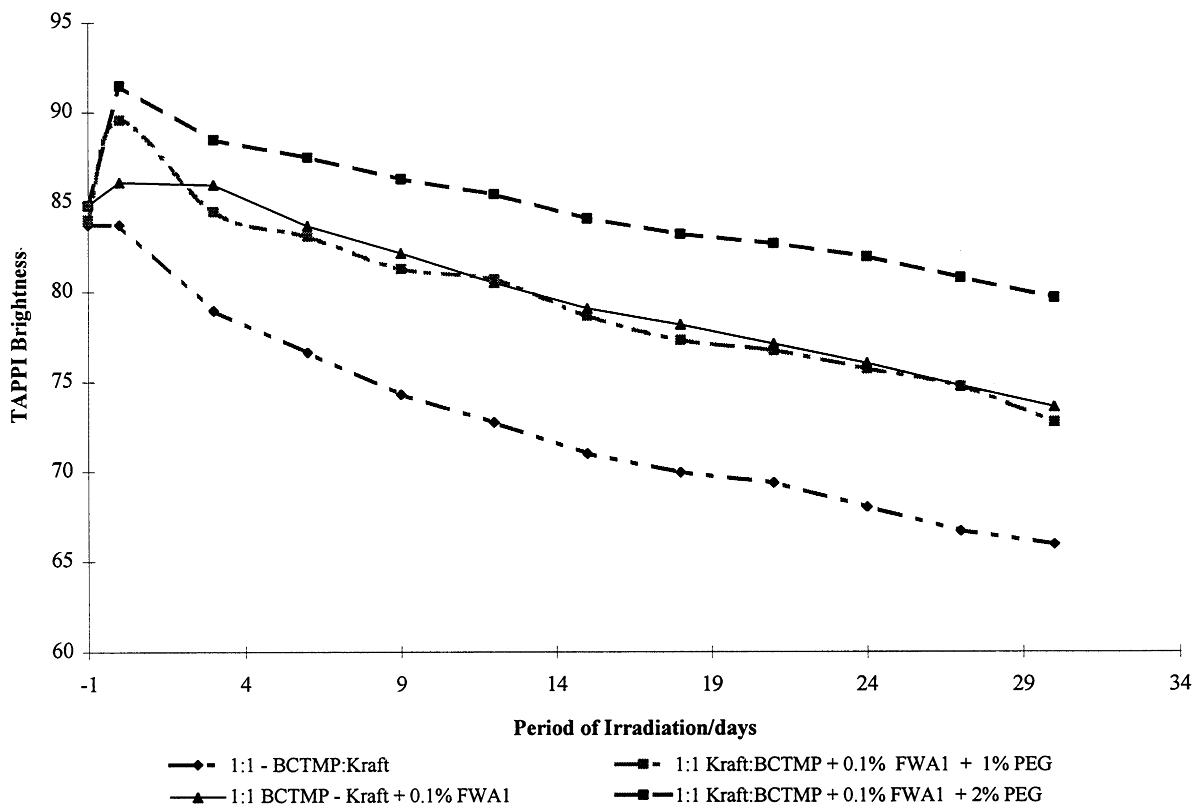


Figure 5. Photoreversion of 1:1 HW BCTMP/SW kraft handsheets treated with FWA1 and PEG.

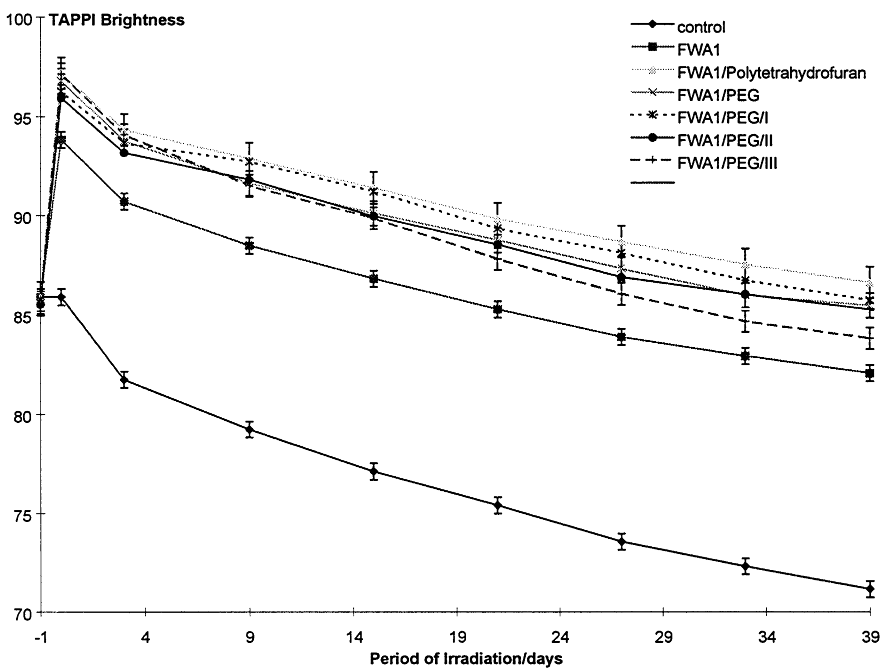


Figure 6. Photoreversion properties of 25% BCTMP/kraft handsheets treated with 1.0% FWA1 and 1.0% PEG, 3.3% polytetrahydrofuran, 1.0% 3-(2-(2-carboxyethythio)ethythio)propanoic acid (I), 1.0% 3-(2-(2-carboxyethythio)methylthio)propanoic acid (II), and 0.5% sulfanylpropanoic acid (III).

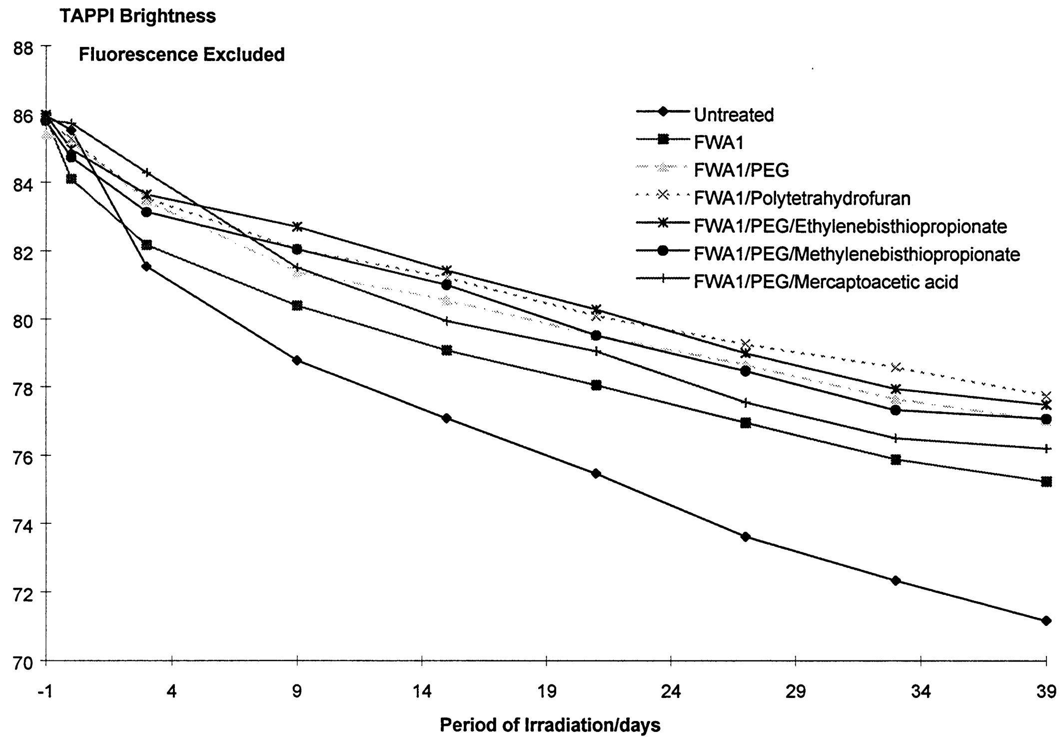


Figure 7. Fluorescent excluded photoreversion properties of 25% BCTMP-kraft handsheets treated with 1.0% FWA1 and 1.0% PEG, 3.3% polytetrahydrofuran, 1.0% 3-(2-(2-carboxyethythio) ethythio)propanoic acid, 1.0% 3-(2-(2-carboxyethythio)methylthio)propanoic acid, and 0.5% 3-sulfanylpropanoic acid.

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